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(54) Title: ARTIFICIAL PATINA

(57) Abstract

The invention relates to an artificial patination formulation and method of coating a copper substrate with an artificial patina. The formulation comprises the reaction product of copper sulfate and optionally iron sulphate, with an inorganic hydroxide compound; and a suitable binder. The invention also relates to a method of coating a copper substrate with an artificial patina comprising contacting the copper substrate with a persulphate solution and then allowing the contacted surface to oxidize in a high humidity atmosphere.

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Title: ARTIFICIAL PATINA

FIELD OF THE INVENTION

This invention relates to an artificial patina for coating copper substrates.

BACKGROUND OF THE INVENTION

When exposed to the atmosphere over time copper substrates develop a stable greenish-blue film known as a patina. Typically, the copper, which is initially bright orange first forms a uniform thin layer of matt brown cuprite (Cu_2O) which is then, over time, coated by a green-blue patina layer of between 5 to 15 micrometre thickness. The nature of the film varies according to the locality of the substrate. Generally, in industrial and urban localities, the patina consists mainly of basic copper sulphate (brochantite $CuSO_4 \cdot 3Cu(OH)_2$) and in marine localities, the patina consists mainly of basic copper chloride (atacamite). At least 4 years, more typically at least 10 years is necessary for the formation of a natural patina coating. In normal city atmospheres a patina will generally form after 8 to 12

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years. In urban atmospheres, the time period is 16 to 20 years.

It is generally regarded that copper substrates coated with a patina are aesthetically pleasing and much use of copper is based on the knowledge that a patina will form. Because of the long period of time required to naturally form a patina, it would be desirable to develop a process and formulation which is capable of forming a patina coating on a copper substrate in a much shorter time.

Hitherto, a number of attempts have been made to develop an artificial patination formulation capable of forming a patina in a short amount of time.

Broadly, these previous formulations can be divided into two groups:

(i) formulations which are applied to the copper substrate as a solution or paste that react with the copper metal to form a patina; and

(ii) formulations which contain a pigment that is applied like a paint and bonds to the copper substrate.

Previous formulations, however, suffer from the disadvantage that none have been capable of producing an artificial patina which matches natural patina in composition and which is stable upon exposure to the atmosphere. The majority of previous artificial patinas peel off after a short time due to poor adhesion of the patina to the metal substrate and special conditions are sometimes required for

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successful formation and bonding of the patina to the metal. Further, in many cases it is necessary to apply a top coat to the patina to prevent loss of the patina.

More specifically, U.S. patent No. 3,152,927 discloses a formulation for an artificial patina which can be applied in the manufacturing plant to produce a pre-patinated copper sheet. These sheets can then be installed at the chosen site. The patination process comprises producing a basic copper nitrate sludge (with excess $\text{Cu}(\text{OH})_2$) which is then applied to oxidised copper sheets and allowed to dry.

The artificial patina coating formed is, however, a basic copper nitrate and is unstable and will undergo competitive reaction to convert the patina to the natural form. This can result in peeling of the applied patina.

Tests by the International Copper Research Association (INCRA project 47c, 1967) revealed that the nitrate patina is not 100% stable with some atmospherically exposed samples performing well in some areas and poorly in others. The initial strength or adhesion of the patina is only moderate with loss of patina occurring at scuff or bend marks due to the brittleness of the coating.

From 1963 to 1967 the International Copper Research Association (INCRA project 47c, 1967) funded a research program to produce an artificial patination

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process. As a result of this work INCRA Patine 60 (b), a solution (paste) of chemicals capable of producing a patina-like coating on copper, was developed. The paste, contains a mixture of copper sulphate, ammonium sulphate, lithium chloride, sodium dichromate, Ben-A-Gel EW and water, and is mixed with hydrochloric acid and then applied to the copper surface with a brush. The patina develops over a few days (and is sensitive to rain or dew during this time). The final patina developed is chemically different to a natural patina and contains various residual chemicals (eg. LiCl) in the coating from the patinating solution. A clear top-coat after application was shown to greatly improve the success rate of the patina.

Disadvantages of this patination process is the expensive chemicals involved and the high labour costs. In addition the reaction time (a few days) is long and can be easily interrupted by natural weather cycles. Results are fairly variable and somewhat unreliable.

The Copper and Brass Research Association (CABRA) ("Artificial Patination" from Copper Roofing CDA Publication No. 57, 1959) developed a spray method for the coating of large copper objects (eg. roofs). The spray solution comprises ammonium sulphate, copper sulphate, ammonia and water. The solution is sprayed onto the surface and allowed to dry. This is repeated five to six times. The development of colour depends

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on suitable weather conditions and rain within eight hours can wash away the solution before the reaction has started. Ideal conditions need fog or a relative humidity of at least 80%.

Disadvantages of this process is that the results of the patination reaction are unreliable and subject to strict atmospheric conditions. In addition the patina formed has a low adhesion and poor weathering qualities.

U.S. Patent No. 3,497,401 describes immersion of copper sheets in an acidic solution (pH = 3.0) containing potassium chlorate (oxidising agent) and copper sulphate. The sheets obtained a patina after about 4 days. This patina is chemically identical to a natural patina but has a different microstructural morphology resulting in easy removal of most of the blue coating. The patina is also a bright blue colour and not the natural blue-green. Major difficulties were experienced in semi-commercial scale production due to the changing solution chemistry (eg. chloride content) of the bath resulting in poor control of the process. The pre-patinated sheets performed well when installed on exposure racks or a roof.

Kobe Steel Ltd (Japan) (Toso Kogaku (Coatings Technology) volume 24 number 7 pages 271-275, 1989) developed a technology allowing the production of an artificial patina in a continuous fashion. The method involves treating a clean plain copper sheet with a

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colouring agent based on basic copper chloride (atacamite). This coloured layer is applied with a roller and an upper layer of water based acrylic emulsion resin is sprayed over the top to ensure adhesion of the colour film. It is believed that this upper layer treatment will disappear with time and that the basic copper chloride coloured layer will react to form the naturally occurring patina.

The artificial patina formed has excellent adhesion properties and can withstand severe metalworking (bending, deep drawing). In addition accelerated corrosion tests and atmospheric exposure tests have indicated that the artificial patina will react to form the naturally occurring compounds.

Disadvantages of this process is the artificial and uniform colour produced. Natural patinas have a blue-green cast and a streaky, mottled appearance. In addition the coating is softer than a natural patina and can be abraded or peeled off due to the continuous acrylic layer.

It is therefore an object of this invention to provide a process and formulation capable of producing a patina which resembles natural patina as closely as possible with regard to composition, morphology and appearance and which has sufficient strength and adhesion over time.

DISCLOSURE OF THE INVENTION

According to a first aspect of the present

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invention, there is provided an artificial patination formulation comprising:

- (a) the reaction product of copper sulphate and optionally iron sulphate, with an inorganic hydroxide compound; and
- (b) a suitable binder.

According to a second aspect of the present invention, there is provided a method of coating a copper substrate with an artificial patina, which method comprises applying to the substrate a formulation according to the first aspect.

According to a third aspect of the invention, there is provided a method of coating a copper substrate with an artificial patina, which method comprises contacting the copper substrate with a persulphate solution, and then allowing the contacted surface to oxidize in a high humidity atmosphere.

PREFERRED EMBODIMENT OF THE INVENTION

The copper substrate can be any copper or copper alloy. The substrate will typically be in fabricated or sheet form which may or may not have been pickled and/or acid-cleaned. In particular, copper sheeting roofing panels manufactured from copper electrosheet are suitable. Copper "electrosheet" is copper cathode prepared by the electrolytic refining of copper anodes.

Preferably, the substrate is oxidized. Typically an aged electrosheet (eg. a four week old electrosheet exhibiting a 3 to 6 micrometer oxide film) will be

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used.

However, if preferred the substrate may be pretreated with an oxidizing procedure.

The formulation can be applied to the copper substrate after installation or can be applied before installation as part of an in-line manufacturing process of the substrate. The formulation can be applied by any suitable application process, typically paintbrush, spray process or by rolling.

Preferably the hydroxide compound is an alkali metal hydroxide such as sodium hydroxide, potassium hydroxide, an alkaline earth metal hydroxide such as barium hydroxide, a transition metal hydroxide or an ammonium hydroxide. Most preferably the hydroxide is sodium hydroxide.

Preferably, the iron sulphate is added in an amount to provide a patina containing up to 10 wt% iron.

Typically, the reaction product is formed by dissolving copper sulphate pentahydrate (eg. 500 g) with iron sulphate heptahydrate (eg. 25 g) in water (eg. 4L), and then adding sodium hydroxide (eg. 1M, 40 g/L, 3.132L) preferably quickly so as to form a fine precipitate. Preferably, the final reaction product has a composition:

$((\text{Cu}_{0.957} \text{Fe}_{0.043})\text{SO}_4)_3((\text{Cu}_{0.957} \text{Fe}_{0.043})(\text{OH})_2)$
which corresponds to a material containing 53.8 wt%

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Cu, 2.1 wt% Fe, 21.2 wt% SO₄ and 22.6 wt% OH. The composition however, can preferably be varied between (CuSO₄)₃(Cu(OH)₂) to ((Cu_{0.8}Fe_{0.2})SO₄)₃((Cu_{0.8}Fe_{0.2})(OH)₂).

A suitable binder includes inorganic silicates preferably water-borne, inorganic silicates such as Zincanode™ 215 available from ICI-Dulux.

Zincanode™ 215 is a high ratio, high build water-borne self curing inorganic silicate.

Typically, 100g to 1,000g of the reaction product is used per 1 litre of binder, more preferably 350g to 450g per litre.

To further assist in adhesion of the formulation to the copper substrate the formulation may further comprise a carboxylic acid. Suitable carboxylic acids include oxalic acid, capric acid, citric acid, tartaric acid, D.L. malic acid, sebamic acid, benzoic acid, succinic acid and stearic acid. Preferably the carboxylic acid is present in an amount from 0 to 1000 ppm based on the total weight of the formulation.

A patina can also be formed by contacting the copper substrate with a strong oxidant such as a persulphate solution. Preferably the solution of persulphate is a solution of sodium or ammonium persulphate (typically containing between 10 and 200 g/L in the pH range 3 to 8). The copper substrate can be contacted by spraying the solution onto the substrate. The contacted surface is then allowed to

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oxidise in high humidity, typically 95% relative humidity by placing the substrate into a humidity cabinet or conducting the process in a natural high humidity environment. An artificial patina on the substrate results. The substrate can then be washed to remove any residual sodium sulphate.

The invention will now be described by way of example only with reference to the following Examples.

EXAMPLE 1

Dissolve 500g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 25g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 4 litres of water. Add 3.1 litres of 1M NaOH (40g/litre) solution. Wash and dry precipitate to produce a "dry" powder. Add 350g of powder to 1 litre of water borne inorganic silicate (Zincanode 215), mix and apply to copper surface.

EXAMPLE 2

Dissolve 500g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 5g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 4 litres of water. Add 2.9 litres of 1M NaOH (40g/litre) solution. Wash and dry precipitate to produce a "dry" powder. Add 650g of powder to 1 litre of water borne inorganic silicate (Zincanode 215), mix and apply to copper surface.

EXAMPLE 3

Dissolve 500g $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and 15g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 4 litres of water. Add 3.0 litres of 1M KOH solution. Wash and dry precipitate to produce a "dry" powder. Add 450g of powder and 100mg oxalic acid to 1 litre of water borne inorganic

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silicate (Zincanode 215), mix and apply to copper surface.

EXAMPLE 4

Dissolve 500g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 7.5g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 4 litres of water. Add 2.9 litres of 1M NH_4OH solution. Wash and dry precipitate to produce a "dry" powder. Add 500g of powder and 100 mg D.L. malic acid to 1 litre of organic silicate (Zincanode 304), mix and apply to copper surface.

EXAMPLE 5

Dissolve 500g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 4 litres of water. Add 3.1 litres of 1M NaOH (40g/litre) solution. Wash and dry (spray dry) precipitate to produce a "dry" powder. Add 350g of powder and 25mg D.L. malic acid to 1 litre of water borne inorganic silicate (Zincanode 215), mix and apply to copper surface.

EXAMPLE 6

Dissolve 50g sodium persulfate in 1 litre of water. Adjust pH to 8 with NaOH. Spray solution onto copper surface. Age for 2 hours in high humidity environment (>95%RH). Allow to dry slowly, then wash surface. Repeated twice; gave desired surface patination.

EXAMPLE 7

Dissolve 10g sodium persulfate in 1 litre of water. Adjust pH to 7 with NaOH. Spray solution onto copper surface. Age for 2 hours in high humidity

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environment (>95%RH). Allow to dry slowly, then wash surface. Repeated ten times; gave desired surface patination.

The processes and formulations of the present invention are suitable for forming a patina on any copper substrate.

CLAIMS:-

1. An artificial patination formulation comprising:
 - (a) the reaction product of copper sulfate and optionally iron sulphate, with an inorganic hydroxide compound; and
 - (b) a suitable binder.
2. A formulation according to claim 1, wherein the hydroxide compound is an alkali metal hydroxide, an alkaline earth metal hydroxide, a transition metal hydroxide or ammonium hydroxide.
3. A formulation according to claim 2 wherein the hydroxide compound is sodium hydroxide.
4. A formulation according to any one of claims 1 to 3 wherein the binder is an inorganic silicate.
5. A formulation according to claim 4 wherein the silicate is a water borne, inorganic silicate.
6. A formulation according to any one of claims 1 to 5 further comprising a carboxylic acid.
7. A formulation according to claim 6 wherein the carboxylic acid is oxalic acid, capric acid, citric acid, tارتic acid, D.L malic acid, sebacic acid, benzoic acid, succinic acid or stearic acid.
8. A formulation according to claim 6 or 7 wherein the carboxylic acid is present in an amount of from 0 to 1000 ppm based on the total weight of the formulation.
9. A formulation according to any one of claims 1 to 8 wherein the reaction product has a composition

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varied between $(\text{CuSO}_4)_3\text{Cu}(\text{OH})_2$ and
 $((\text{Cu}_{0.8}\text{Fe}_{0.2})\text{SO}_4)_3((\text{Cu}_{0.8}\text{Fe}_{0.2})(\text{OH})_2)$.

10. A formulation according to any one of claims 1 to 9 containing 100 to 1,000 g of reaction product per litre of binder.

11. A method of coating a copper substrate with an artificial patina, comprising applying to the substrate a formulation according to any one of claims 1 to 10.

12. A method according to claim 11 wherein the copper substrate is copper or a copper alloy.

13. A method according to claim 11 or 12 wherein the substrate is in fabricated or sheet form which has optionally been pickled and/or acid cleaned.

14. A method according to any one of claims 11 to 13 where the substrate is copper electrosheet.

15. A method according to any one of claims 11 to 14 wherein the substrate is oxidized prior to application of the formulation.

16. A method according to any one of claims 11 to 15 wherein the formulation is applied by paintbrush, spraying or by rolling.

17. A method according to any one of claims 11 to 16 wherein the formulation is applied after installation or before installation as part of an in-line manufacturing process of the substrate.

18. A method of coating a copper substrate with an artificial patina comprising contacting the copper

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substrate with a persulphate solution and then allowing the contacted surface to oxidize in a high humidity atmosphere.

19. A method according to claim 18 wherein the persulphate solution contains sodium or ammonium persulphate.

20. A method of claim 18 or 19 wherein the persulphate solution contains between 10 g/L to 200 g/L of the persulphate.

21. A method according to any one of claims 18 to 20 wherein the persulphate solution has a pH from 3 to 8.

22. A method according to any one of claims 18 to 21 wherein the persulphate solution is applied by spraying.

23. A method according to any one of claims 18 to 22 wherein the relative humidity of the atmosphere is 95%.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 95/00236

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.⁶ C09D 1/02, 1/00, 7/12; C23C 22/52, 22/63, 22/68

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC C09D 1/02, 1/00, 7/12; C23C 22/52, 22/63; C23F 7/02Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above.Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT: copper or cupric (C09D): persulpat or persulfat (C23)
JAPIO: copper or cupric (C09D): persulphat or persulfat (C23)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	AU 24531/77 (503411) <u>A</u> (SERISUI KAGAKU KOGY) <u>26 October 1978</u> Page 7, Examples 1-8, Claims 1-6	18-23
X, Y	Derwent Abstract Accession No. 40329C/23, Classes A 82, G02, M13, JP 55-054361 <u>A</u> (DOWA MINING CO LTD (JAPS)) <u>21 April 1980</u> Abstract	1-3, 10-17
X	Derwent Accession No. 88040473/06, Classes A82, E32, G02, JP 63-000373 <u>A</u> , (KUBOKO PAINT K K (SHIN)) <u>5 January 1988</u> Abstract	1-3, 10-17

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
	21 JUNE 1995 (21.06.95)
Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA	<i>Grant McNeice</i>
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 95/00236

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	Derwent Abstract Accession No. 23310E/12, Class J01, JP 55-102868 <u>A</u> , (MATSUSHITA ELEC WORKS) <u>16 February 1982</u> . Abstract	18-23
A, Y	AU 55126/80 (532049) <u>A</u> (JOHNSON S D) <u>6 August 1981</u> Pages 4, 8, 9	1-5,11-17
A, Y	US 3972845 <u>A</u> (KANSAI PAINT COMPANY LTD) <u>3 August 1976</u> Columns 5, 9 and 10	1-3,11-17
A	Derwent Abstract Accession No. 88-053874 Classes A60, E32, G02, A17, JP 1-153811 <u>A</u> , (MITSUBISHI RAYON K K) <u>18 January 1988</u> . Abstract	1,11-17

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 95/00236

Box I **Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)**

This international search report has not established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claim Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Invention 1: Apply copper sulphate and inorganic hydroxide and binder to copper or copper alloy substrate. Patination composition therefore.

Invention 2: Apply persulphate solution to copper or copper alloy surface and expose to high humidity to produce artificial patina.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/

AU 95/00236

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
AU	24531/77	DE IT	2718288 1081377	FR JP	2349805 52131236	GB US	1556902 4195124
AU	55126/80						
US	3972845	AT FR JP	8928/74 2278744 51010836	DE GB NL	2452466 1476461 7414558	ES IT US	431733 1039515 3972845
END OF ANNEX							